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The Origin of Ultrasonic Absorption in Water*

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The origin of the excess ultrasonic absorption in water is sought in a lag in the rearrangement of the molecules during an acoustic compression. An expression is derived for such structural absorption in a liquid, and an approximate calculation is made for the case of water which agrees reasonably well with the experimental excess absorption over the temperature range 0° to 80°C. A relaxation treatment is applied to the structural component of compression on the assumption of two molecular states of packing. The acoustic wave alters the equilibrium distribution of molecules between the two states by perturbing molecular transitions to and from the sites of closer packing through the work performed by or against it in the volume change accompanying the transition. The activation energy determining the rate of transition should be close to that for shear viscous flow and the configuration of closer packing approximately that of closest packing. The relaxation time associated with the process is found to be of the order of 10^{-12} second for water. This mechanism implies an isothermal bulk viscosity coefficient for liquids, which in the case of water has a magnitude several times that of shear viscosity.

1. INTRODUCTION

In liquids, as in gases, the observed absorption of ultrasonic waves is far too great to be explained by shear viscosity or heat conduction processes. For gases the excess absorption has found its explanation in heat capacity lag—a slowness in the exchange of energy between external and internal molecular degrees of freedom. The numerical importance of this process for liquids has not yet been evaluated for want of a determination of the relaxation time for the energy transfer independent of absorption measurements. In gases a measurable dispersion in sound velocity furnishes the means for such an independent determination, but no dispersion, in general, has been detected in liquids.

For water, however, heat capacity lag has been excluded as the possible explanation of the excess ultrasonic absorption. Herzfeld[1] has shown the magnitude of the absorption and the absence of dispersion to be inconsistent with this hypothesis, and, more recently, absorption measurements over a temperature range show a continued large absorption through 4°C, where with the minimum in specific volume the specific heat at constant volume and at constant pressure are equal, the sound propagation becomes isothermal, and the heat capacity lag effect should vanish.[2]

2. MOLECULAR VIEW OF COMPRESSION

A molecular view of compression in a liquid suggests a structural mechanism for absorption. During acoustic compression the molecules of the liquid are brought uniformly closer together and also rearranged or repacked more closely. The former process, molecular compression, resembles that which occurs in crystals, is relatively rapid, and may be considered instantaneous and in phase with the applied pressure. The latter, configurational or structural compression, involves the breaking of intermolecular bonds or flow past energy barriers which stabilize the equilibrium configuration; it proceeds at a finite rate comparable with the period of the ultrasound and hence lags the applied pressure appreciably. It is relaxational and leads to absorption.

3. PHENOMENOLOGICAL ASPECTS

The presence of both instantaneous and relaxational compressibilities in a medium may be expressed by the dynamical stress-strain differential equation

$$\dot{s}=\frac{\beta_0 P-s}{\eta\beta_0}+\beta_\infty\dot{P}=\frac{s_0-s}{\tau}+\beta_\infty\dot{P}, \qquad (1)$$

where $s=\Delta V/V$ is the relative compression, β_∞ is the instantaneous compressibility (the effective value for frequency $\nu\rightarrow\infty$), β_0 is the total or static compressibility (for $\nu\rightarrow 0$), and η is the bulk viscosity coefficient. $\beta_0 P=s_0$ is the equilibrium

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[1] K. Herzfeld, J. Acous. Soc. Am. **13**, 32 (1941).

[2] F. Fox and G. Rock, Phys. Rev. **70**, 68 (1946).

value of compression approached for an applied constant pressure, P. The expression

$$\eta\beta_0 = \tau \tag{2}$$

gives the relaxation time (the time required for the compression to reach $1/e$th of its equilibrium value under an applied constant pressure). The dot over a symbol indicates time differentiation. For a harmonic pressure, $P = P_0 e^{i\omega t}$, the solution of Eq. (1) is

$$s = \left(\beta_\infty + \frac{\beta_r}{1+i\omega\tau}\right)P, \tag{3}$$

where

$$\beta_r = \beta_0 - \beta_\infty \tag{4}$$

is the relaxational compressibility. The effective compressibility is therefore

$$\left(\beta_\infty + \frac{\beta_r}{1+i\omega\tau}\right). \tag{5}$$

Omitting the effect of shear viscosity, which within negligible terms is additive, the square of the velocity of a wave in a relaxational medium may therefore be written formally

$$c^2 = \frac{1}{\rho\left(\beta_\infty + \dfrac{\beta_r}{1+i\omega\tau}\right)}, \tag{6}$$

(where ρ is the density) and is complex. Resolved into real and imaginary parts, it is

$$c^2 = \left\{\frac{\beta_0 + \omega^2\tau^2\beta_\infty}{\rho(\beta_0{}^2 + \omega^2\tau^2\beta_\infty{}^2)} + i\frac{\omega\tau(\beta_0 - \beta_\infty)}{\rho(\beta_0{}^2 + \omega^2\tau^2\beta_\infty{}^2)}\right\}. \tag{7}$$

For a damped plane wave, $\xi = \xi_0 e^{-\alpha x}\cdot e^{i\omega(t-x/v)}$, the amplitude absorption coefficient, α, and the real phase velocity, v, are easily derived from c^2. For $\omega\tau \ll 1$, which proves to be the case here (τ is found to be of the order of 10^{-12} second), the expression for the modified absorption coefficient, $2\alpha/\nu^2$, is found from Eq. (7) to be

$$2\alpha/\nu^2 = \frac{4\pi^2}{v}\cdot\beta_r\tau/\beta_0 = \frac{4\pi^2}{v}(1-\beta_\infty/\beta_0)\tau. \tag{8}$$

When heat capacity lag is negligible, the ratio $\gamma = C_p/C_v$ is equal to its ordinary real value. For water, which is the liquid of interest here, $\gamma = 1$ within a few percent in the range to be considered; hence $\beta_{\mathrm{ad}} = \gamma\beta_{\mathrm{iso}} \cong \beta_{\mathrm{iso}}$, and no numerical distinction need be made between adiabatic and isothermal compressibilities.

4. MOLECULAR ASPECTS OF STRUCTURAL RELAXATION

To derive molecular expressions for β_0 and τ, a relaxation treatment may be applied to the configurational component of compression. The simple assumption of a relaxation process (heat capacity relaxation) with two energy states has provided the most usable results for gases, and the possibility of a two-state representation will be assumed here. To each molecule two states will be assumed available: state 1, characterized by larger volume and lower energy, and state 2, characterized by smaller volume and higher energy. Compression occurs through a relative increase in the number of molecules in state 2. Upon application of an acoustic pressure, a molecule initially in state 1 may flow or jump to a site of closer packing, associated with higher energy state 2. Let n_1 and n_2 be the numbers of molecules in states 1 and 2, respectively, and k_1 and k_2 be the transition rates per molecule for transitions 1–2 and 2–1. Considering one mole of liquid, $n_1 + n_2 = N$, Avogadro's number. The transition or reaction equation is

$$-\dot{n}_2 = k_2 n_2 - k_1 n_1. \tag{9}$$

For small amplitudes the sound radiation perturbs the equilibrium rates and populations to first-order terms only. Hence

$$-\Delta\dot{n}_2 = k_{20}\Delta n_2 + n_{20}\Delta k_2 - k_{10}\Delta n_1 - n_{10}\Delta k_1, \tag{10}$$

where the subscripts, 0, indicate equilibrium values, but have been omitted from the pertubations. Since the variations are assumed to be harmonic, time differentiation in Eq. (10) may be replaced by multiplication by $i\omega$. Δk_1 can be expressed in terms of Δk_2 through the use of the following equilibrium relations:

$$\dot{n}_2 = 0, \quad n_{10}k_{10} = n_{20}k_{20}. \tag{11}$$

By the Boltzmann distribution law

$$n_{20}/n_{10} = \frac{e^{-F_2/kT}}{e^{-F_1/kT}} = e^{-\Delta F/kT}, \tag{12}$$

where F_1 and F_2 are the free energies per molecule associated with the states 1 and 2, $\Delta F = F_2 - F_1$, and k, as usual, in Boltzmann's constant. Also since $n_1 + n_2 = N = \text{constant}$, $-\Delta n_1 = \Delta n_2$. Δk_1 and Δn_1 may then be eliminated from Eq. (10), and the perturbation in n_2 is found to be

$$\Delta n_2 = \frac{-k_{20} n_{20} \Delta(\Delta F/kT)}{i\omega + k_{10} + k_{20}}. \tag{13}$$

Hence the average number of molecules which jump to states of closer packing because of an isothermal increase in pressure, ΔP, will be

$$\Delta n_2 = \frac{-k_{20} n_{20} [\partial(\Delta F)/\partial P] \cdot \Delta P}{kT(i\omega + k_{10} + k_{20})}. \tag{14}$$

This expression may be put into the more convenient form

$$\Delta n_2 = \left\{ \frac{-N \cdot [\partial(\Delta F)/\partial P] \cdot \Delta P}{2kT(1 + \cosh \Delta F/kT)} \right\} \cdot \frac{1}{1 + i\omega/(k_{10} + k_{20})}. \tag{15}$$

The compressibility, defined by $(-1/V)(\partial V/\partial P)$, may be expressed in terms of $\Delta n_2/\Delta P$ by writing it as

$$\frac{-1}{V} \frac{\partial n_2}{\partial P} \cdot \frac{\partial V}{\partial n_2} = \beta'.$$

Then

$$\beta' = \frac{1}{V} \left(\frac{\partial V}{\partial n_2} \right) \left\{ \frac{N \cdot [\partial(\Delta F)/\partial P]}{2kT(1 + \cosh \Delta F/kT)} \right\} \frac{1}{1 + i\omega\tau}, \tag{16}$$

where τ has been written for $1/(k_{10} + k_{20})$.

In the potential diagram for two adjoining energy states shown in Fig. 1, F_1 and F_2 are the free energy levels of states 1 and 2. The activation energy required for a molecule to jump from state 1 to state 2 is ΔF_1^*, and for the reverse transition is ΔF_2^*. The pressure dependent part of the difference between the free energies, $F_2 - F_1 = \Delta F$, is $-P \cdot \Delta v_m$, where Δv_m is the effective diminution in volume per molecule involved in the transition 1–2. Therefore, $\partial(\Delta F)/\partial P = -\Delta v_m$. The term $\partial V/\partial n_2$ is simply the effective change in volume per molecule transition 1–2 and is thus equal to $-\Delta v_m$. Upon substitution of these equivalents and introducing the notations: $\Delta V = N \cdot \Delta v_m$ = the difference in molal volume of states 1 and 2; $kT = R$, the molal gas constant; re-interpreting ΔF and all other free energy symbols to refer to one mole instead of one molecule, the expression for the compressibility β' becomes

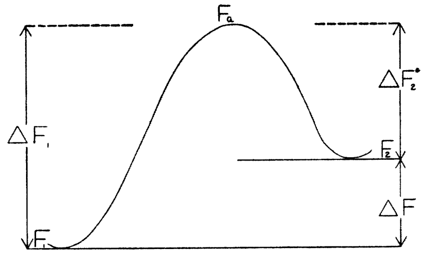

FIG. 1. Potential diagram for two adjoining energy states.

$$\beta' = \left\{ \frac{V(\Delta V/V)^2}{2RT(1 + \cosh \Delta F/RT)} \right\} \frac{1}{1 + i\omega\tau} = \frac{\beta_r}{1 + i\omega\tau}. \tag{17}$$

5. EVALUATION OF THE RELAXATION TIME

From the theory of absolute reaction rates,[3] the expression for a reaction or transition rate may be written

$$k_j = \frac{kT}{h} e^{-\Delta F_j^*/RT}, \tag{18}$$

where h is Planck's constant, k is Boltzmann's constant, and ΔF_j^* is the free energy of activation per mole required for the process. This expression is applicable to a process involving the rearrangement of matter, regarded either as a chemical or mechanical process. Applying Eq. (18) to the evaluation of the specific rate constants, k_1 and k_2, and using the relation $\Delta F_2^* = \Delta F_1^* - \Delta F$ (see Fig. 1), the expression for the relaxation time, $\tau = 1/(k_{10} + k_{20})$, is

$$\tau = \frac{h}{kT} \cdot \frac{e^{\Delta F_1^*/RT}}{1 + e^{\Delta F/RT}}. \tag{19}$$

6. RELATION BETWEEN SHEAR AND COMPRESSIVE FLOW

In both shear and compressive flow of a viscous liquid the molecules flow or jump past neigh-

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[3] Glasstone, Laidler, and Eyring, *Theory of Rate Procesess* (McGraw-Hill Book Company, Inc., New York, 1941).

boring molecules into adjoining sites. In both cases energy bonds are broken with the immediate neighbors, and the activation energies for the two flows should be of the same order of magnitude. It is true that in terms of the model, molecules in both states 1 and 2 would flow in shear flow, whereas in compressive flow only molecules in state 1 flow. If it is assumed that the activated state for flow is the same for both types of flow and if most of the molecules are in state 1, then the activation energy for shear viscous flow $\Delta F^*_{\text{vis}} \approx \Delta F_1^*$. Provisionally this will be assumed. An allowance for the number of molecules in state 2 might be made by taking

$$\Delta F^*_{\text{vis}} = \frac{n_1}{N}\Delta F_1^* + \frac{n_2}{N}\Delta F_2^*. \tag{20}$$

In the present case this is found to make ΔF_1^* about 6 percent higher than ΔF^*_{vis} at 0°C. In view of the uncertainties involved, however, the value of such a correction is questionable.

Since a molecular relaxational approach has been applied to ordinary shear viscosity,[3, 4] there is at hand a means of evaluating the activation energy required for molecular flow, independent of ultrasonic absorption data. Eyring's expression for the shear viscosity coefficient is

$$\mu = \frac{hN}{V} e^{\Delta F^*_{\text{vis}}/RT}, \tag{21}$$

where V is the molal volume and the other symbols have the usual meanings. The relaxation time may therefore be written in terms of μ:

$$\tau = \left\{ \frac{V}{RT(1+e^{\Delta F/RT})} \right\} \mu. \tag{22}$$

7. STRUCTURE OF WATER

Water has been characterized as having a broken-down ice structure, where the long-range order has disappeared, but considerable local order persists. X-ray studies of the ice state indicate that each water molecule has four nearest neighbors, tetrahedrally arranged around it, a very open structure. This tetrahedral coordination is maintained by intermolecular hydrogen bonds, consisting principally of strong dipole forces. Similar studies of water show that the coordination with nearest neighbors still tends to be tetrahedral, but is more irregular, with changing rather than permanent neighbors, and an average of three to two hydrogen bonds present over the range from 0° to 100°C. Bernal and Fowler[5] have approximated the x-ray diffraction curve for water by combining the curve for regular tetrahedral, quartz-like structure with the curve for a simple close-packed liquid (approximately closest possible packing). The notion of water as a mixture of two structures, one open and one compact, while scarcely definitive, is frequently held and is suggestive for the present purpose.

In the two-state model for water, state 1 may be identified with a state which is more ice-like and state 2 with a state more like that of a simple close-packed liquid. For instance, it may be

TABLE I. Absorption coefficient—calculated and experimental values.

							$2\alpha/\nu^2$ (10^{-17} sec.^{2}/cm)		
							Theoretical		
T (°C)	V (cm^3)	v (10^{-5} cm/sec.)	β_0 (10^{-12} cm^2/dyne)	μ (millipoise)	τ (10^{-12} sec.)	η (millipoise)	$\beta_\infty=15$ $\times10^{-12}$	$\beta_\infty=18$ $\times10^{-12}$	Experimental
0	18.02	1.40	50.8	17.94	4.05	80	80	74	79.6
4	18.02	1.43	50.2	15.68	3.49	70	68	63	—
5	18.02	1.43	49.9	15.19	3.37	68	65	59	61.4
10	18.02	1.45	47.8	13.10	2.86	60	54	49	49.5
20	18.05	1.48	45.8	10.09	2.14	47	38	35	34.3
30	18.09	1.51	44.7	8.00	1.64	37	28	25	25.9
40	18.16	1.53	44.2	6.53	1.30	29	22	20	19.5
50	18.23	1.54	44.1	5.49	1.08	24	18	16	16.0
60	18.33	1.55	44.3	4.70	0.89	21	15	14	13.8
70	18.42	1.55	44.6	4.07	0.75	17	12	11	11.6
80	18.54	1.55	45.1	3.57	0.64	14	11	10	10.6

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[4] J. Frenkel, *The Kinetic Theory of Liquids* (Clarendon Press, Oxford, 1946).

[5] J. D. Bernal and R. H. Fowler, J. Chem. Phys. 1, 515 (1933).

considered that the majority of water molecules are three-bonded and a minority are two-bonded. Such a view accords with the fact that the average percent of bonding near 0°C is about 70 percent[6] and the free energy difference between the two states in the present application comes out to a value which is estimated as a half-bond per molecule. (The energy of one bond is shared by two molecules.) Provisionally it will be considered that most of the molecules are in state 1, which is associated with a molal volume, V_1, lying between that of water and ice, and that state 2 is associated with a molal volume, V_2, given by closest packing, but not necessarily with the absence of all the bonds.

8. RELATIVE CHANGE IN VOLUME

Water molecules may be considered spherical of radius, a, for packing computation. The molal volume for closest packing of equal spheres is $V=N\cdot 4\cdot 2^{\frac{1}{2}}\cdot a^3$, where N is Avogadro's number. Near 0°C the average distance of closest approach of molecules in water is 2.90A.[7] Using this value as the packing diameter, the molal volume for state 2 is $V_2=10.4$ cm^3. The molal volume for state 1, lying between that of water and ice, is between 18.0 cm^3 and 19.6 cm^3. This gives for the relative change in volume, $\Delta V/V$, a value between 0.42 and 0.51. The average value, $\Delta V/V=0.47$, will be used.

9. INSTANTANEOUS AND RELAXATIONAL COMPRESSIBILITIES

Since the potential energy of a water molecule is determined principally by nearest neighbors in both states, the instantaneous compressibility of water should be comparable in magnitude with the compressibility of ice, but somewhat larger. Near 0°C the adiabatic compressibility of ice has been determined as 10×10^{-12} cm^2/dyne (dynamic method) and at -7°C there is a static determination giving the value of 12×10^{-12} cm^2/dyne for the isothermal compressibility.[8] Taking into account nearest neighbors only, the instantaneous compressibility of water can also be calculated from intermolecular potential functions for water molecules. Using the potential function for bonded molecules, determined by Cross, Leighton, and Burnham[9] in a study of Raman scattering of water and ice, a compressibility of 12×10^{-12} cm^2/dyne is obtained. From a potential function for molecules free to rotate, developed by Margenau and Myers[10] primarily for high temperatures, a value of 24×10^{-12} cm^2/dyne is found. For the instantaneous compressibility of water, two trial values, 15×10^{-12} and 18×10^{-12} cm^2/dyne, will be adopted.

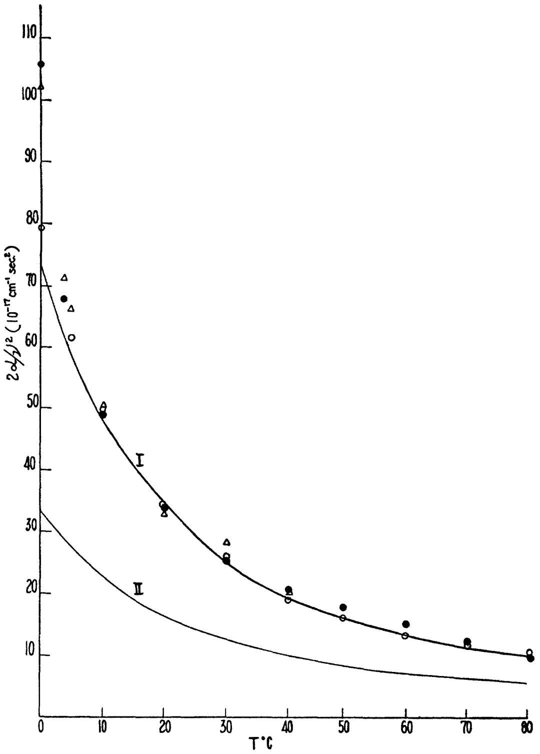

FIG. 2. *I*—Theoretical structural absorption (with $\beta_\infty=18\times10^{-2}$ cm^2/dyne). Experimental excess absorption: ○—J. M. Pinkerton; ●—Smith and Beyer; △—Fox and Rock. *II*—Theoretical shear viscosity absorption.

10. FREE ENERGY DIFFERENCE OF THE TWO STATES

From the relation between β_r and ΔF determined by Eq. (17) with the use of the above numerical values, ΔF is calculated to be 0.5 kcal.

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[6] R. H. Ewell and H. Eyring, J. Chem. Phys. **5**, 726 (1937).

[7] J. Morgan and B. E. Warren, J. Chem. Phys. **6**, 666 (1938).

[8] R. Dorsey, *The Properties of Water Substance* (Am. Chem. Soc. Mono. Ser. No. 81, Reinhold Publishing Corporation, New York, 1940).

[9] Cross, Burnham, and Leighton, J. Am. Chem. Soc. **59**, 1134 (1939).

[10] H. Margenau and V. Myers, Phys. Rev. **11**, 307 (1944).

per mole of half-bonds. From the viscosity study by Ewell and Eyring,[6] a rough estimate of the free energy of a hydrogen bond in water can be made. The value is also found to be about 0.5 kcal. per mole of half-bonds, suggesting that states 1 and 2 differ by a hydrogen bond.

11. COMPUTATION OF THE ABSORPTION

There is no way to estimate quantitatively the temperature variations of the two compressibilities, but β_∞ should increase with temperature due to both thermal expansion of the liquid and to structural changes. For constant ΔF, the term $(1+e^{\Delta F/RT})$ appearing in expression (22) for the relaxation time decreases with temperature (about 4 percent from 0° to 20°C). In their effect on the absorption coefficient (cf. Eq. (8)) these two influences tend to nullify each other, and both will be taken as constant.

Table I gives the values of the relaxation time, bulk viscosity, and the intensity absorption coefficient computed as functions of temperature from Eqs. (22), (2), and (8), respectively. Experimental values of excess absorption taken from pulse measurements of J. M. Pinkerton,[11] and estimated accurate within a few percent, are included for comparison. (By experimental "excess absorption" is meant the observed value less the calculated absorption due to shear viscosity.) Data not otherwise acknowledged are taken from R. Dorsey, *The Properties of Water Substance.*[8]

In Fig. 2 is given the curve for the theoretical absorption computed with $\beta_\infty = 18\times 10^{-12}$ cm^2/dyne and a plot of the experimental values of the excess absorption. In addition to the measurements of J. M. Pinkerton, those of Smith and Beyer[12] and those of Fox and Rock[2] are given. The latter two sets are by radiation pressure methods. The curve for the calculated absorption resulting from shear viscosity is included for comparison.

12. DISCUSSION AND CONCLUSIONS

The absorption calculated theoretically for structural relaxation agrees sufficiently well with the excess ultrasonic absorption observed experimentally, reproducing its temperature variation over the range 0° to 80°C within 10 percent or better. The theory requires the numerical values of any two of the three quantities, β_∞, $\Delta V/V$, ΔF. While only approximate estimates of these quantities can be made at present, reasonable variations continue to give results of the correct magnitude.

It is of interest to note that the theoretical relaxation time arrived at, $\tau \sim 10^{-12}$ second, is consistent with the observed absence of velocity dispersion in thermally originated hypersound of the frequency range of 10^{10} cycles per second. The presence of two compressibilities, molecular (instantaneous) and structural, explains qualitatively the existence of a minimum in the static or total compressibility experimentally observed for water near 40°C. The instantaneous or molecular compressibility can be expected to show the usual continuous increase with temperature, but the structural compressibility will decrease from 0° to 40°C with the breaking of hydrogen bonds, which takes place mainly in that interval. The simultaneous presence of a decreasing component and an increasing component which eventually predominates leads to a minimum. Structural relaxation implies for all liquids an isothermal coefficient of bulk viscosity. For water this coefficient is several times greater than that of ordinary shear viscosity.

Liquids of small viscosity can be divided into a relatively low absorption group in which the ratio of the observed absorption to the shear viscosity absorption is small, i.e., from 2 to 4, and a high absorption group for which this ratio is of the order of 10 to 100. The associated or hydrogen-bonded liquids like water and alcohols fall into the first group,[13] and it is very likely that structural relaxation or bulk viscosity is the mechanism responsible for the observed excess absorption in all of these liquids. For the second group, the isothermal bulk viscosity, while appreciable, would seem insufficient to account for the very high absorption. Heat capacity relaxation may well be the responsible mechanism for this group which shows high absorption, and appears to be comprised of non-associated

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[11] J. M. Pinkerton, Nature **160**, 128 (1947), and private communication.

[12] M. Smith and R. Beyer, Brown University, private communication.

[13] C. Kittel, J. Chem. Phys. **10**, 614 (1946).

liquids. It is to be expected that this latter process would be more important in non-associated liquids where there is little coupling of molecules to facilitate the transfer of internal vibrational energy, leading to a relatively large relaxation time.

Structural relaxation may be expected to play a role in any high frequency process. A possible application may be to shock wave phenomena, where high frequency components are present. It may prove useful also to use absorption data to evaluate the structural molecular quantities involved in the derived expressions.

ACKNOWLEDGMENT

It is a pleasure to thank Professor R. B. Lindsay, who suggested the problem, for his constant interest and stimulating discussion, and for the careful criticism and supervision he rendered. I also wish to thank L. Tisza, B. E. Warren, H. Margenau, and K. F. Herzfeld for helpful discussion on topics related to the work.

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On Dirac's Theory of Continuous Spectra

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By an heuristic application of the group generated, in a formal sense, by the quantum-mechanical rule of commutation, Dirac has arrived at the following result: The group property "propagates" an eigenvalue, discrete or continuous, in such a way as to compel its emergence at any preassigned eigenvalue. Dirac's deduction is somewhat highhanded from the mathematical point of view and, what is worse, even the final result happens to be false in general. It is shown, however, below that the idea which seems to underly Dirac's argument can be saved to some extent. To this end, Dirac's assertion will be reformulated so as to become both consistent and probable. It turns out that what is needed for such a re-interpretation is the substitution of "pieces of band spectra" in lieu of Dirac's unspecified "spectra." The proof, carried out only for the case of wave equations of radial symmetry depends on the completeness of the orthogonal system formed by the eigenfunctions and eigendifferentials together.

I.

THE formal structure of a familiar argument of Dirac,[1] aiming to prove that all quantum-mechanical operators are bound to contain every value between $-\infty$ and $+\infty$ in their spectra, consists of two propositions:

(i) $\epsilon=\epsilon_0$ is in the spectrum for *some* ϵ_0, if ϵ denotes a point of the line on which *possible* eigenvalues are marked, and

(ii) the presence of an ϵ_0 "infects" every region on the line $-\infty<\epsilon<\infty$ so strongly that every ϵ is bound to be an ϵ_0.

The lack of mathematical rigor in this deduction is criticized in the physical literature.[2] That not even the final result can be correct without appropriate reservations, the nature of which is not revealed by Dirac's deduction, is shown by the decisive counter example of periodic potentials (one-dimensional lattices). Needless to say, there is nothing wrong in the assumption of (i), and so the trouble must come from the argument leading to (ii), simply because too much is taken for granted in what more or less[3] corresponds to the Hilbert space of the mathematicians.

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[1] P. A. M. Dirac, *The Principles of Quantum Mechanics* (The Clarendon Press, Oxford, 1935), (2nd ed.), pp. 93–94.

[2] E. K. Kemble, *The Fundamental Principles of Quantum Mechanics* (McGraw-Hill Book Company, New York and London, 1937), pp. 298–299.

[3] Many of the customary misunderstandings result from a common origin of central significance; namely, from the omission of any specification of the range of functions on which the operator is supposed to be defined. For example, just because Dirac's "unitary operator" (see reference 1), say $\exp(iR)$, which appears to be generated by an infinitesimal group (of unspecified range), is something that happens to "correspond" to a number of unit absolute value, there is no justification for applying the operator on a range on which the formal series becomes divergent.

It is worth mentioning that the lacunae in the continuous